Table 1. Final positional parameters with standard deviations for the non-hydrogen atoms and possible positional parameters for the hydrogen atoms. The numbering of the hydrogen atoms, *cf.* Fig. 1.

Atom			
Cl	0.0647(2)	0.0094(4)	0.4981(2)
N(1)	0.2475(8)	0.5123(15)	0.4345(4)
N(2)	0.4122(9)	0.9458(17)	0.3678(5)
C(1)	0.2441(9)	0.5712(15)	0.3450(5)
C(2)	0.1587(12)	0.4190(19)	0.2942(6)
C(3)	0.1505(12)	0.4790(23)	0.2099(6)
C(4)	0.2301(13)	0.6893(22)	0.1794(7)
C(5)	0.3194(12)	0.8447(21)	0.2305(6)
C(6)	0.3290(11)	0.7853(17)	0.3153(6)
H(2)	0.097	0.235	0.312
H(3)	0.110	0.393	0.184
H(4)	0.211	0.704	0.114
H(5)	0.380	1.008	0.221
H(11)	0.185	0.320	0.448
H(12)	0.222	0.637	0.460
H(13)	0.340	0.482	0.450
H(21)	0.445	0.854	0.421
H(22)	0.496	1.082	0.343

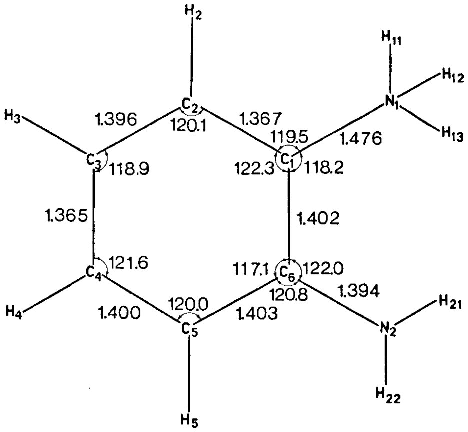

Fig. 1. Bond lengths (Å) and angles (°) in the aromatic molecule. The mean standard deviations are 0.013 Å and 0.8°, respectively.

are normal with carbon-nitrogen distances ($C-NH_2$) of 1.39(1) Å and ($C-NH_3^+$) of 1.48(1) Å. The chloride ion is surrounded by three cations (Fig. 2). Each cation is coordinated *via* the $-NH_3^+$ group through hydrogen bonds $N-H\cdot\cdot\cdot Cl$. The $N-Cl$ distances are 3.15(1) Å, 3.15(1) Å, and 3.17(1) Å. The shortest $N-Cl$ distance from an $-NH_2$ group is 3.43(1) Å.

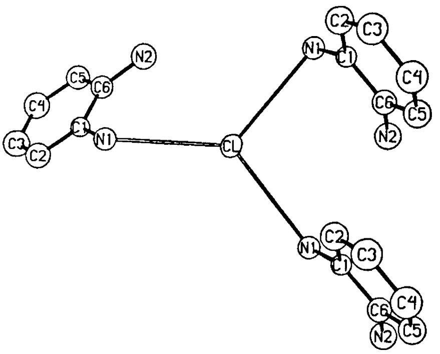

Fig. 2. The three cations $C_6H_4N_2H_5^+$ hydrogen bonded to the chloride ion.

In order to obtain a more detailed information of the hydrogen bonding system a neutron diffraction study of the compound has been started. A full report of this work will be published later. A list of observed and calculated structure factors is available on request to the author.

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Received August 7, 1972.

Studies on Orchidaceae Alkaloids. XXXV.* Alkaloids from *Hammarbya paludosa* (L.) O.K. and *Liparis keitaoensis* Hay.

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Recently the isolation of two alkaloids from *Hammarbya paludosa* (L.) O.K.

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* For paper XXXIV, see Ref. 1.

was reported.[2] The structure of one of these alkaloids, paludosine, was given. We here report the structure of the minor alkaloid, for which we propose the name hammarbine (I).

The alkaloid was obtained as an amorphous solid. Acid methanolysis gave *inter alia* lindelofidine, identified as its acetate [3] and 2,2-dimethyl-6-methoxycarbonyl-8-methoxychroman (II), indistinguishable from an authentic sample obtained by methylation of 2,2-dimethyl-8-methoxychroman-6-carboxylic acid.[4] A small amount of methyl 4-hydroxy-3-methoxy-5-(3-methoxy-3-methylbutyl)benzoate (III), identified by its mass spectrum, was also isolated.

Acid hydrolysis of I gave glucose, which was reduced with sodium borohydride and the resulting glucitol characterised as its hexaacetate by GLC–MS.[5,6] Methylation of I followed by acid hydrolysis, reduction, and acetylation produced 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol.[7] The optical rotation of I is the same as that of paludosine.[2] It is concluded that I differs from paludosine only in the substitution pattern of the aromatic nucleus. It is therefore suggested that I is a *β*-D-glucopyranoside.

Two alkaloids related to hammarbine were isolated from *Liparis keitaoensis* Hay. in the usual manner *via* their reineckeates. We propose the name keitaoine (IV) and keitine (V) for the major and minor alkaloid respectively. They occur in the ratio 2 : 1 in the crude alkaloid mixture.

Acid methanolysis of IV have II, III, and laburnine. Acid hydrolysis gave glucose characterised as above. Methylation analysis [7] and application of Hudson's isorotation rules show that IV is a *β*-D-glucopyranoside.

No glucose or other sugar was obtained on acid hydrolysis of V, but II, III, and laburnine were isolated after acid methanolysis. We therefore suggest that V has the structure given in Fig. 1.

Alkaloid V was not obtained when pure IV was subjected to the same conditions as existed during the isolation of the alkaloids from the plant extract, which demonstrates that V was not formed from IV during the isolation. The possibility that IV has been formed from V by *post mortem* enzymatic hydrolysis is, however, not excluded.

Experimental. The UV, IR, and NMR spectra were recorded as previously described.[2] The mass spectra were recorded on a Perkin-Elmer 270 spectrometer and a LKB 9100 spectrometer.

Characterisation of hammarbine (I). Fresh plants* (320 g) of *Hammarbya paludosa* gave a total yield of 70 mg of I as an amorphous solid $[\alpha]_D^{23}+9$(*c* 0.31, ethanol). UV spectrum (ethanol), λ_{max} *nm* (log *ε*): 290 (3.93), 248 (3.91). Mass spectrum, *m/e* (rel. intensity): M^+ 521 (0.2), 397 (13), 192 (12), 137 (16), 124 (100), 83 (90).

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* Collected near Stocholm, Sweden.

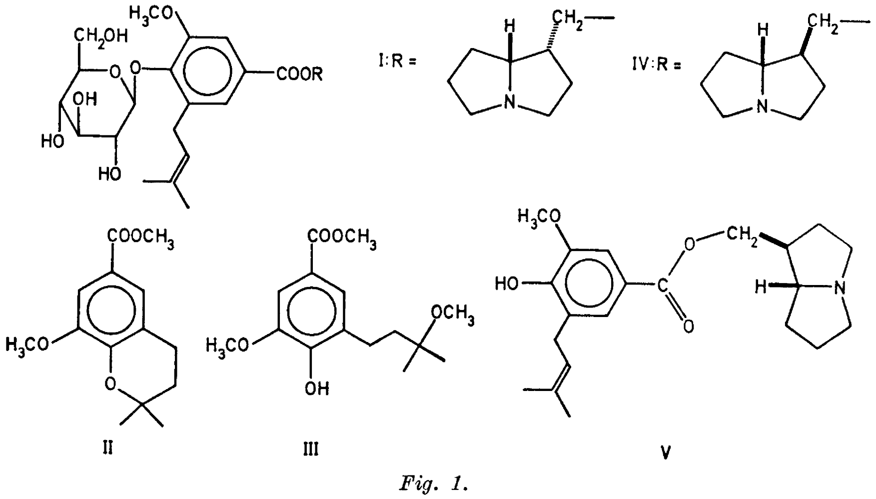

Fig. 1.

Acid methanolysis of I. A solution of the alkaloid (38 mg) in methanol (15 ml) and sulphuric acid (0.1 ml) was heated under reflux for 64 h. After concentration to 2 ml and addition of water (10 ml), the solution was extracted with chloroform (2 × 5 ml). The combined chloroform solutions were dried (Na_2SO_4) and gave after evaporation 2,2-dimethyl-6-methoxycarbonyl-8-methoxychroman (II, 12.5 mg) and methyl 4-hydroxy-3-methoxy-5-(3-methoxy-3-methylbutyl)benzoate (III, 2 mg). Compounds II and III were separated on a 20 % SE-52 Chromosorb AW DMCS column (3 mm × 2 m) using nitrogen as carrier gas. Compound II, identical with the methanolysis product, was obtained by methylation of the corresponding acid[4] as colourless crystals, m.p. 68 – 70°. UV spectrum (ethanol), λ_{max} nm (log ε): 296 (infl), 270 (4.05), 225 (4.24); IR spectrum ($CHCl_3$): σ_{max} 1710 (s), 2820(w) cm^{-1}; NMR spectrum ($CDCl_3$), τ: 2.4 – 2.6 (m, 2 H), 6.10 (s, 6 H), 7.17 (t, 2 H, $J = 7$ Hz), 8.17 (t, 2 H, $J = 7$ Hz), 8.60 (s, 6 H); mass spectrum, *m/e* (rel. intensity): M^+ 250 (57), 219 (19), 195 (100), 191 (12), 163 (21), 91 (5), 77 (7).

Mass spectrum of III, *m/e* (rel. intensity: M^+ 282 (5), 267 (2), 250 (56), 219 (8), 195 (100), 191 (10), 163 (18), 91 (6), 73 (31).

The acidic aqueous phase was made alkaline (pH 12) and extracted with chloroform (6 × 10 ml). After evaporation of the dried (Na_2SO_4) chloroform solution the amino alcohol was obtained as a colourless oil (12.5 mg) $[\alpha]_D^{23} + 60°$ (*c* 0.32, ethanol). An ethereal solution of the alcohol was treated with ketene and the product was identified as lindelofidine acetate by comparison with an authentic sample (GLC, MS).[3]

Acid hydrolysis of I. 10 mg of the alkaloid was dissolved in sulphuric acid (0.25 M, 5 ml) and the solution kept at 90° for 2 h. The solution was neutralized ($BaCO_3$), evaporated to 1 ml and reduced with sodium borohydride. The resulting glucitol was acetylated and the hexaacetate identified by GLC – MS.[5,6]

Methylation and hydrolysis of I. The alkaloid (10 mg) was methylated with methyl iodide and dimethyl sulphinyl sodium in dimethyl sulphoxide.[7] The methylated alkaloid was hydrolysed and acetylated, giving 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol which was identified by GLC – MS [7].

Isolation and characterisation of keitaoine (IV) and keitine (V). From fresh plants * (155 g) of *Liparis keitaoensis* a crude alkaloid mixture (660 mg) was obtained by the usual extraction procedure. IV and V were separated on a column of neutral alumina (Brockman II – III). Compound V was eluted with chloroform and IV with water-methanol (1 : 1). The water-methanol fraction was concentrated and then made alkaline and extracted with chloroform. The combined chloroform solutions were dried (Na_2SO_4) and the solvent evaporated. Keitaoine (IV) was obtained as an amorphous solid, $[\alpha]_D^{23} - 13°$ (*c* 0.8, ethanol). UV spectrum (ethanol), λ_{max} nm (log ε): 293 (3.36), 255 (3.85); IR spectrum (KBr): σ_{max} 1720(s) cm^{-1}. (Found: C 62.0; H 7.73; N 2.52; O 27.43. Calc. for $C_{27}H_{39}NO_9$: C 62.2; H 7.54; N 2.69; O 27.61.)

Keitine (V) was obtained as an amorphous solid, $[\alpha]_{578}^{23} - 7°$ (*c* 0.6, ethanol). Mass spectrum, *m/e* (rel. intensity): M^+ 359 (19), 342 (2), 236 (3), 219 (4), 163 (5), 140 (3), 124 (100), 95 (17), 83 (61), 55 (39).

Acid methanolysis of IV and V was carried out as described above for alkaloid I and gave II, III, and laburnine, $[\alpha]_D^{23} + 16$ (*c* 0.3, ethanol) further characterised as its acetate.[3]

Acid hydrolysis and methylation analysis were carried out as described for I.

Acknowledgements. We thank Dr. Jörgen Lönngren and Dr. Ragnar Ryhage for measuring the mass spectra and Miss Britt-Marie Sjöberg for collecting *Hammarbya paludosa.* We thank Dr. Svante Brandänge for valuable suggestions and Dr. Arnfinn Meidell for a sample of 2,2-dimethyl-8-methoxychroman-6-carboxylic acid.

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Received August 16, 1972.

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* Collected by Chow Cheng Orchids, Taichung, Taiwan.